Liquid crystal acrylate-based networks: polymer backbone–LC order interaction

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Abstract

New synthetic pathways to poly- and monodomain acrylate-based networks via gamma-irradiation and chemical crosslinking are described. Strain-induced orientation transitions and phase behavior are studied by X-ray scattering, differential scanning calorimetry and optical microscopy. Analysis of the observed phenomena is given in terms of crosslinking conditions, network topology, structure and spatial distribution of crosslinks. The pretransitional behavior and the observed shifts in clearing point Tn–i are in good agreement with theoretical predictions. The reorientation process in monodomain networks is regulated via strain gradients generated by external mechanical field. The variation in geometrical shape of the samples gives an opportunity to control and realize two different reorientation mechanisms: uniform director rotation and reorientation via stripe domains. Gamma-irradiation is found to be a powerful tool for fixation of any current distribution of poly- and monodomain regions within the LC film. 'Macroscopic memory' of the information recorded on the films is observed and discussed. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Liquid crystal; Elastomer; LC network; Crosslinking; Monodomain; Nematic director; Reorientation

1. Introduction

Anisotropic crosslinked systems with LC properties represent an area of research in the field of self-assembling materials, which are of fundamental interest and technological potential. Liquid crystal elastomers [1–4] occupy an important position within the wide range of crosslinked materials because they combine the basic features of polymer elastomers with the anisotropy of physical properties of liquid crystals, and as previously suggested [5] represent 'the new state of matter'. This paper gives a review of our recent data related to the following problem: to what extent it is possible to control phase behavior, state of LC order and macroscopic alignment in mesogen-containing elastomers by varying the crosslinking conditions, structure of crosslinks, network topology and external mechanical field.

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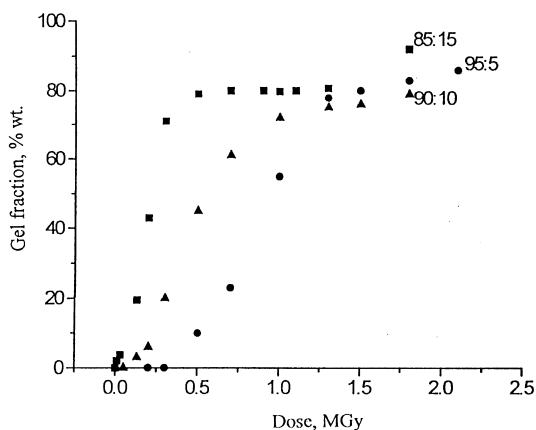
Coming back to the main goal of this paper, one has to formulate the definition of cross-linking conditions. First of all it is the phase state of the original linear polymer that can be crosslinked either below or above the nematic-to-isotropic phase transition temperature T_{n-i}. It implies the fixation of different conformations of macromolecule: an isotropic coil (crosslinking carried out in isotropic melt) or an anisotropic coil (crosslinking in LC phase) (Fig. 1).

Based on the modern theoretical approach and general ideas describing the structure of crosslinked materials one should take into consideration at least two important points.

According to theory the nematic order and

T_{n-i} of the resultant crosslinked system depend on the state of order of the starting linear polymer during the crosslinking reaction. On the other hand, the crosslinking agent molecule being incorporated in the mesophase can act as a defect deteriorating the LC ordering. From the experimental viewpoint it means that to estimate the network nematic field interaction and separate it from the effect of defects we have to search for the system where the destructive role of crosslinks can be weakened by the variation of the crosslinking approach. Thus, the second variable condition could be the type of crosslinking and the structure of the network junction, which may be introduced by reactive agent or under radiation of different types (Fig. 2).

Using as an example the linear nematic side chain acrylic copolymers having the following structure:

we will discuss two different approaches: crosslinking under the action of gamma-irradiation and crosslinking by means of reactive agents,

Fig. 1. Schematic representation of the coil anisotropy transformation with the change in temperature.

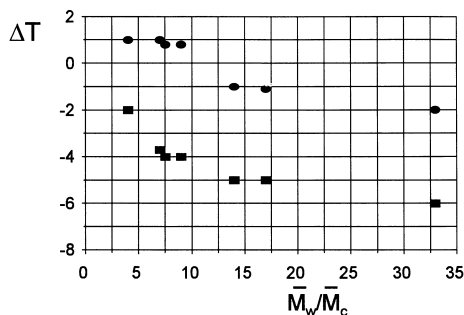Fig. 2. Scheme of the crosslinking process carried out with crosslinking agents or induced by γ-rays.

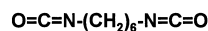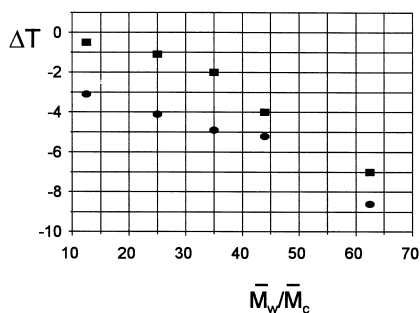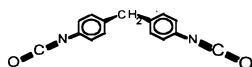Fig. 3. Gel-fraction as a function of radiation dose for copolymers containing different amounts of hydroxyethylacrylate units (5, 10, 15 mol.%).

ethylacrylate (HEA) units in macromolecules of CN-biphenyl-containing polyacrylates results from the task to compare two independent crosslinking approaches. The hydroxyl group acts as the crosslinking point during the chemical reaction with diisocyanates and simultaneously the presence of 2-hydroxyethylacrylate units considerably affect the sensitivity of the copolymer to gamma-rays comparatively to that of LC homopolymer [6,7]. The observed strong tendency of the copolymers gel-dose to decrease with increasing the content of HEA (Fig. 3) proves the idea that these units participate in gamma-induced crosslinking reaction as such.

namely, 4,4′-methylenediphenyl diisocyanate (MDI) and 1,6-hexamethylene diisocyanate (HMDI). The idea to introduce 2-hydroxy-

2. Results and discussion

Fig. 4 compares samples crosslinked below and above the clearing point Tn–i. It is neces-

Fig. 4. Deviation in the Tn–i phase transition temperature as a function of the crosslinking density.

sary to point out that independently of the type of crosslinking, either by crosslinking agents or via gamma-irradiation, networks prepared in the isotropic phase show the decrease in the clearing point comparatively to that of starting copolymer as it is predicted by theory [8]. Alternatively, if samples are crosslinked in the nematic phase their thermal behavior depends on the type of crosslinking. MDI as a crosslinking agent causes the decrease in the clearing point. Contrary to that, an increase in Tn–i is observed for gamma-crosslinked materials. As for HMDI agent it occupies an intermediate position between the two systems just mentioned. It slightly increases Tn–i at the low crosslink density, whereas at a certain value of $\overline{M}_w/\overline{M}_c$ the decrease in clearing point occurs.

Thus, the difference in ΔT $(\overline{M}_w/\overline{M}_c)$ curves observed even for chemically crosslinked systems may be considered as a proof of coupling between the nematic order and phase behavior of networks, although the distorting role of defects still influences the properties of the systems. On the other hand, gamma-induced crosslinking gives a unique opportunity to eliminate the destructive effect of crosslinks and to isolate the coupling effect between the nematic field and network anisotropy.

Simultaneously with the change in phase transition temperature one may observe the effect of the structure and topology of networks on the pretransitional phenomena [9]. The static Kerr effect is known to be a powerful tool for the analysis of pretransitional phenomena in the isotropic phase close to Tn–i [10,11]. Application of electric field to the linear copolymer as well as to crosslinked samples in the isotropic phase results in linear increase in the induced birefringence with the square of the applied electric field. As an example, this is shown in Fig. 5 for the gamma-crosslinked network at different temperatures. These data indicate the validity of the Kerr law for both linear and crosslinked systems within the whole temperature and electric field ranges studied. The Kerr constant B estimated from the slope of linear
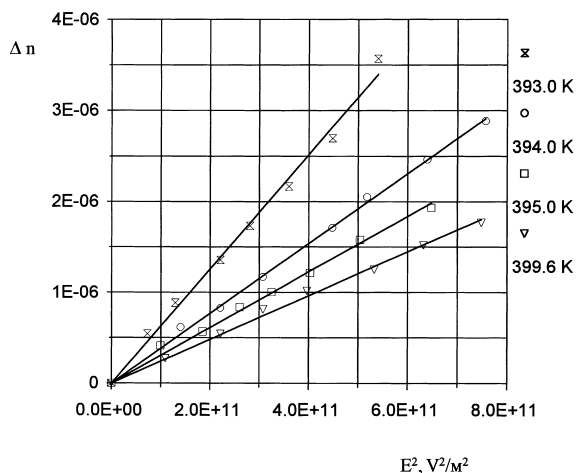

Fig. 5. Birefringence as a function of the electric field intensity for a sample crosslinked by γ-rays ($\overline{M}_w/\overline{M}_c = 11.6$).

curves has a positive value and increases with decreasing temperature when approaching the clearing point (Fig. 6). The divergence of the Kerr constants and the linearity of the curves for the reciprocal Kerr constants as a function of temperature are in good agreement with the Landau-de Gennes theory [12]. In the framework of this theory the Kerr constant depends on $(T - T*)^{-1}$. Therefore, we can describe the pretransitional phenomena in linear copolymer as well as in differently crosslinked networks in terms of the fluctuations critical behavior that
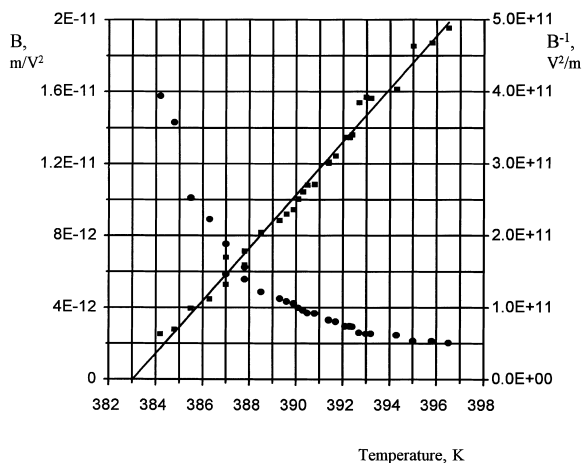

Fig. 6. Kerr (■) and reciprocal Kerr constant (●) as a function of temperature for the linear copolymer prior to crosslinking.

indicates the presence of nematic phase. Qualitatively speaking, nothing happens after the introduction of crosslinks into the linear nematic copolymer. Nonetheless, the interpolated hypothetical $T*$ values are strongly different: it is much lower for chemically crosslinked material than for the gamma-crosslinked one (Fig. 7). In general, all thermodynamic fluctuations of the nematic order parameter are strongly suppressed by the interaction with the elastic network. It is usually the effect of quenched non-thermal effects, like defects, which are much stronger in chemically crosslinked material as previously discussed.

This is also proven by the estimations of the correlation radius of fluctuations (Fig. 8). The
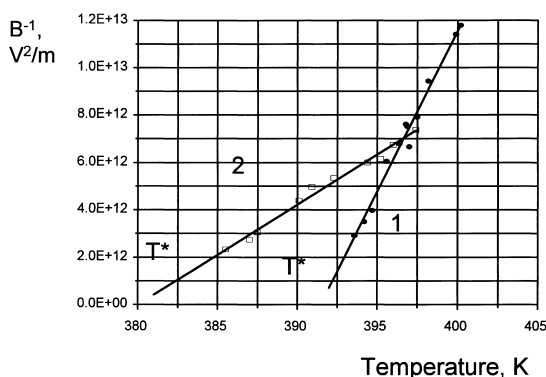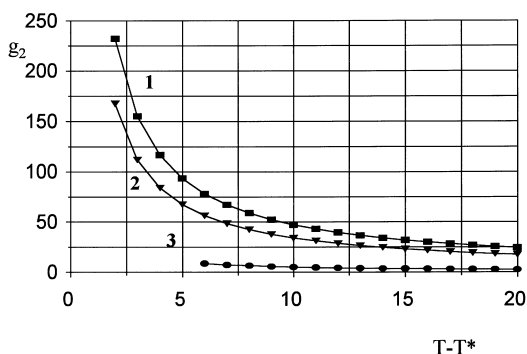
strong increase in the Kerr constant in the vicinity of isotropic-nematic phase transition results from the increase in the fluctuation correlation radius. The value of g_2 is defined through the following equation [13]

$$g_2 = 1 + \sum_{i,j} (1/2)(3\cos^2\theta_{ij} - 1)$$

where θ is an angle between the main molecular axes of i and j molecules.

In the first approximation one may consider g_2 as a number of mesogenic units which reorient in correlated fashion. The correlation parameter diverges at $T*$ and attains a value about several hundreds in the vicinity of Tn–i for a linear copolymer and gamma-crosslinked sample that is in good correlation with data known for side chain polymers [14]. However, this value is much lower for chemically crosslinked material, and this again correlates with the idea of strong defects introduced by chemical crosslinking reaction.

If it is true, the orientation order parameter should be also sensitive to the change in the network topology and structure of the network junction. It comes from X-ray measurements [15] which give the most important information on the orientation behavior of LC elastomers. The comparison of gamma- and chemically crosslinked materials shows the following. Increase in the crosslink density ($\overline{M}_w/\overline{M}_c$) practically does not influence the upper value of S for gamma-crosslinked materials although the normal stress at which S attains the upper value is greater for samples with the higher density (Fig. 9a).

Contrary to these elastomers, networks prepared via chemical crosslinking with MDI as a reactive agent are influenced by the crosslink density to that extent that the upper level of the parameter S decreases with increasing the $\overline{M}_w/\overline{M}_c$ value (Fig. 9b). At low temperature the order parameter is the same for both types of materials having equal crosslink density. However, the temperature curves for S are completely different (Fig. 10). With the increase in

Fig. 7. Reciprocal Kerr constant versus temperature for a sample crosslinked by γ-rays (1) and MDI (2); $\overline{M}_w/\overline{M}_c = 11.6$.

Fig. 8. Correlation parameter g_2 vs. temperature for the linear copolymer (1) and samples crosslinked by γ-rays (2) and MDI (3).
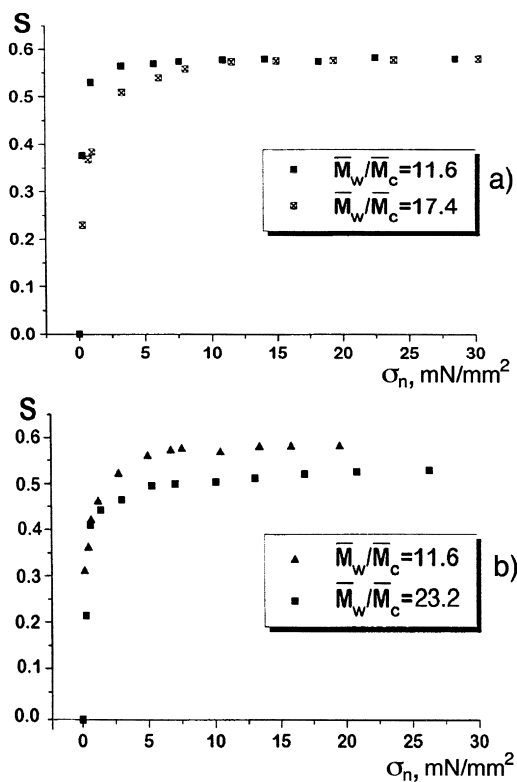
Fig. 9. Orientational order parameter versus normal stress for γ-crosslinked samples (a) and for samples crosslinked by MDI (b) at $T_{red} = 0.953$.
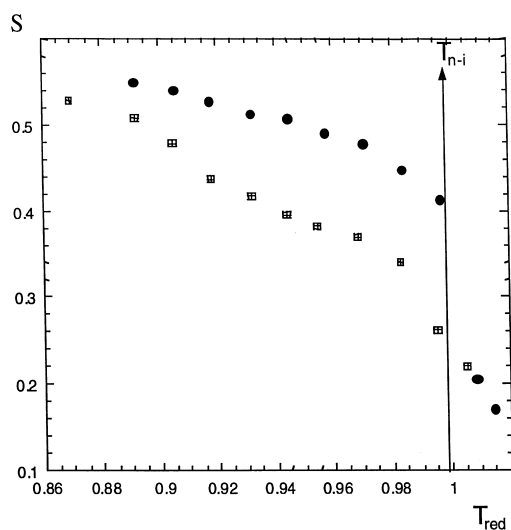

Fig. 10. Orientational order parameter versus temperature for γ-crosslinked sample (●) with $\overline{M}_w / \overline{M}_c = 11.6$ and for the sample crosslinked by MDI ($\overline{M}_w / \overline{M}_c = 23.2$). External mechanical field $\sigma_{ext} = 4$ mN/mm^2.

temperature S goes down within the broad temperature range for chemically crosslinked with MDI samples, whereas gamma-crosslinked networks show a sharp drop in the S value in the vicinity of T_{n-i}.

So the whole set of different experiments shows the strong sensitivity of the thermodynamic behavior and orientational order to the structure of the network junction points and more importantly to the network topology or spatial distribution of crosslinks. First of all, one has to summarize the experimental facts.

1. One and the same units (HEA) in macromolecules contribute in the crosslinking process.
2. Structure of the network junctions should be essentially different. In the networks prepared with the crosslinking agents it is a rigid bulky fragment of MDI molecule or flexible residue of HMDI. Under the action of gamma-irradiation network junctions should be formed by recombination of the radicals generated in the system.
3. The increase in crosslink density $\overline{M}_w / \overline{M}_n$ within the wide range from 2 to 25 does not affect either the clearing point, nor the order parameter in gamma-crosslinked materials.
4. The shift in T^* and the radius of fluctuation correlations do not show strong sensitivity to gamma-crosslinking comparatively to starting copolymer, whereas they change in the 'chemically' prepared networks.

Now one may assume that, because of marked difference between the structures of mesogenic and non-mesogenic groups (HEA), the linear copolymer contains microregions with the increased concentration of different units. Therefore, irradiation leads to the formation and accumulation of the crosslinks in the microregions enriched with HEA units. These regions 'shield' the network junctions from the mesogenic groups and do not allow them to function as defects deteriorating the nematic field. As a result, these crosslinks function only

as the elements that stabilize the nematic (ir-radiation in the liquid crystal) or isotropic (crosslinking at $T > T$n–i) phases. As for the chemically crosslinked systems, in which the junctions are formed through the fragments of crosslinking agent the difference in their thermal behavior compared to gamma-crosslinked materials may be caused by two reasons. First, the molecules of crosslinking agent MDI are fairly large in size and have a very rigid structure. As a result, complete 'shielding' of these junctions is not realized. Second, it is easy to notice that the chemical structures of MDI and mesogenic fragments are to some extent similar. Therefore, the molecules of crosslinking agent can penetrate into the microregions with the increased concentration of mesogenic fragments, which contain some amount of reactive hydroxyl groups. This tendency should increase with the rise in the concentration of crosslinks. This is embodied in the sharp drop in Tn–i with increasing the crosslink density.

Networks containing HMDI fragments as junction points occupy an intermediate position because groups may not have the same compatibility with the LC phase as MDI does and should not heavily destroy the LC order. How-ever, at higher densities the deteriorating role of network junctions prevails though it is not that strong.

The combination of two crosslinking approaches gives the opportunity to create the liquid single crystal elastomers (LSCE) or monodomain networks. At T above the glass transition temperature one can stretch the polydomain film and induce the uniaxial orientation that may be fixed by cooling the system below T_g [16,17]. This makes the acrylate-based materials different from siloxane elastomers [18,19]. The 'frozen' orientation can be additionally fixed by gamma-rays. The strong sensitivity of LC elastomers to the action of mechanical stress allows one to control over the nematic director orientation [20]. If the monodomain sample is stretched in the direction normal to the original LC director orientation one may observe either uniform rotation of the nematic director [21] or the reorientation involving the formation of stripe domains [22]. There was contradiction between the two different mechanisms described for the reorientation phenomena which one tried to explain in terms of the difference in chemical structure and, as a result, different network anisotropy. We have
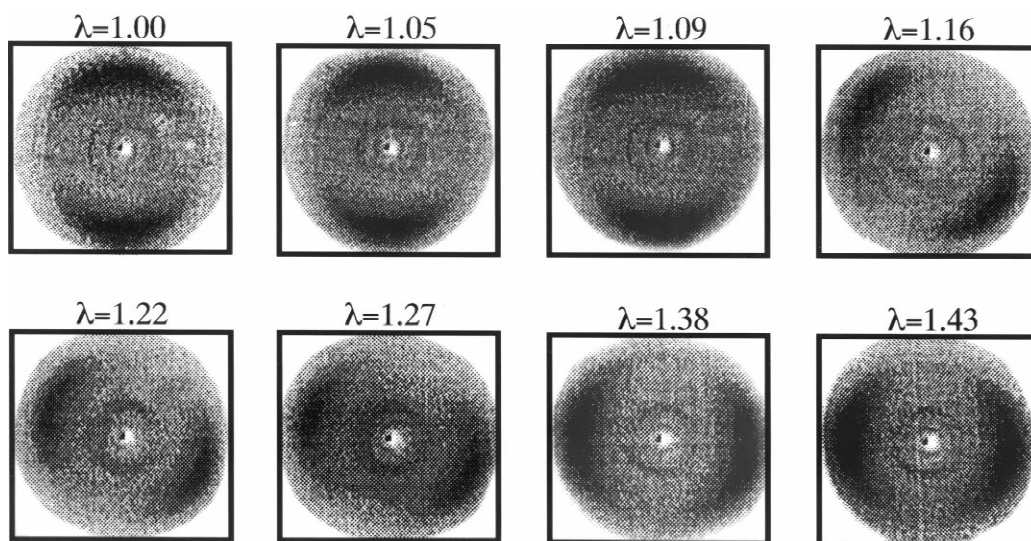

Fig. 11. X-ray diffraction patterns collected from the center of the monodomain film (initial aspect ratio AR = 12) at different strain. The external mechanical field is applied perpendicular to the original director, $T = 90°$C.

succeeded in overcoming this disparity by finding that geometrical shape (aspect ratio) of the monodomain films drastically affects the dynamics and mechanism of the reorientation transition. Uniform continuous rotation of the director occurs in narrow samples with the aspect ratio (AR)=12 when the external mechanical field is applied perpendicular to the initial director. This is clearly seen from the set of X-ray patterns (Fig. 11) that indicate the continuous rotation of the textured X-ray diffraction maxima at wide angles. Under the same conditions, films with AR=2.5 demonstrate the formation of stripe domains with alternating sense of director rotation (clockwise and counter-clockwise towards the stress axis). The change in the X-ray pattern from two reflections

to four ones and back to two-fold diffractogram (Fig. 12) gives the idea of the stripe domains formation which has also been proven by optical observations.

The deformation of the square optically transparent film generates the opaque area in the geometrical center of the sample. It is divided into two opaque spots with the stretching which then moves along the stress axis from the center of the film towards the clamped edges as the deformation proceeds (Fig. 13a). As it comes from the X-ray diffraction analysis the scattered areas correspond to the stripe domains, whereas a uniform continuous rotation is observed in the other regions of the film (Fig. 13b).

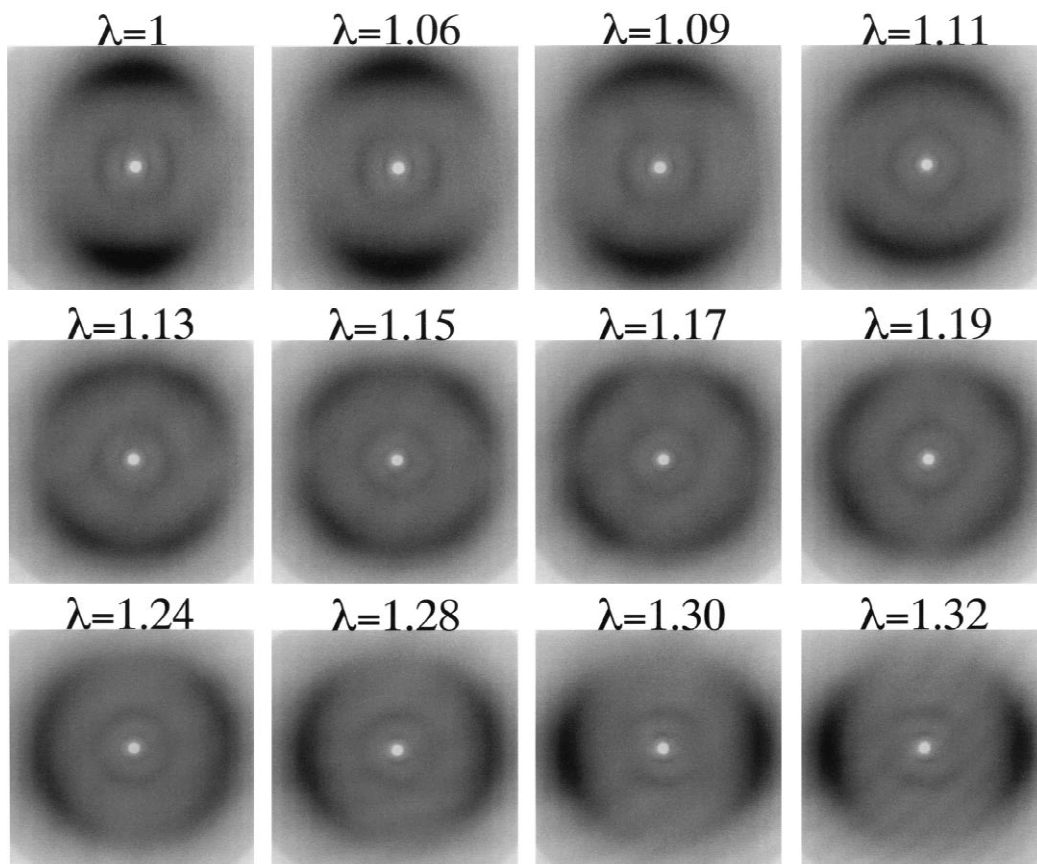The phenomena described above prove the possibility to control the LC director reorienta-

Fig. 12. X-ray diffraction patterns collected from the center of the monodomain film initial aspect ratio AR=2.5) at different strain. The external mechanical field is applied perpendicular to the original director, $T=90$°C.
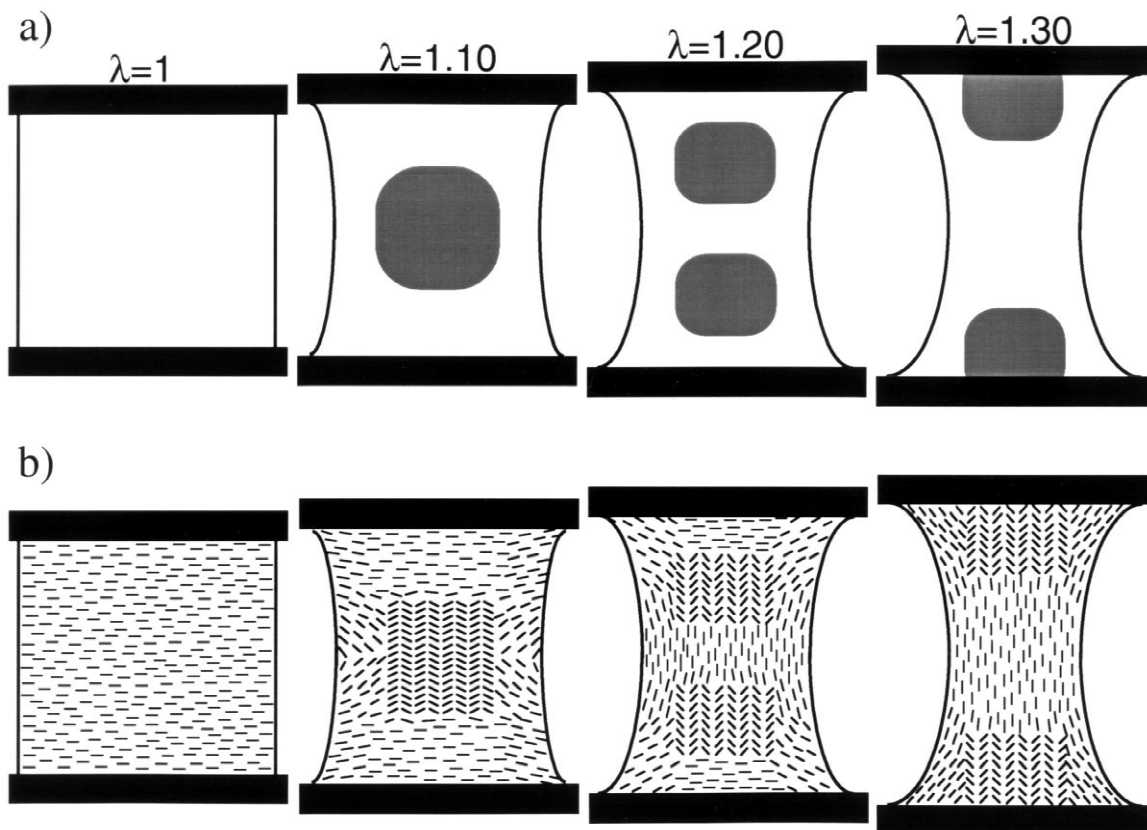
Fig. 13. Schematic representation of the square monodomain film exposed to different strain. Black circles show opaque regions formed in the optically transparent sample after deformation (a). The rods indicate the direction of local alignment of the mesogens (b).

tion and as a result the optical properties of the monodomain network by carrying the shape of the sample. One may guess that this is not the shape itself but the inhomogeneous distribution of the external mechanical field within the stretched film, which is responsible for the mechanism of the director reorientation.

In terms of technological potential, the most important property of monodomain networks is related to 'memory effect' which was initially observed in acrylate-based systems [23,24]. It was found that the original direction of orientation and order parameter S completely restore after the monodomain film undergoes phase transition from isotropic state to nematic phase. We explored this interesting phenomenon using gamma-irradiation approach which turned out to be a very effective tool for locking in place any

given distribution of director within the LC films. Fig. 14 displays the schematic route that allows one to record symbol information in these systems. The transformation of the mono-domain sample into isotropic state is followed by complete disappearance of the macroscopic alignment of mesogens. The external mechanical load applied in certain regions can create adhesive contacts between the isotropic film and the substrate. After subsequent cooling of the film (below T_g) the monodomain structure does not restore in these regions because the internal mechanical field is very weak and cannot overcome the adhesion force. As a result, the isotropic director distributor existing at $T > T$n–i is frozen in these areas. In other words, they acquire the polydomain structure and become opaque at temperatures below T_g. Simultaneous-
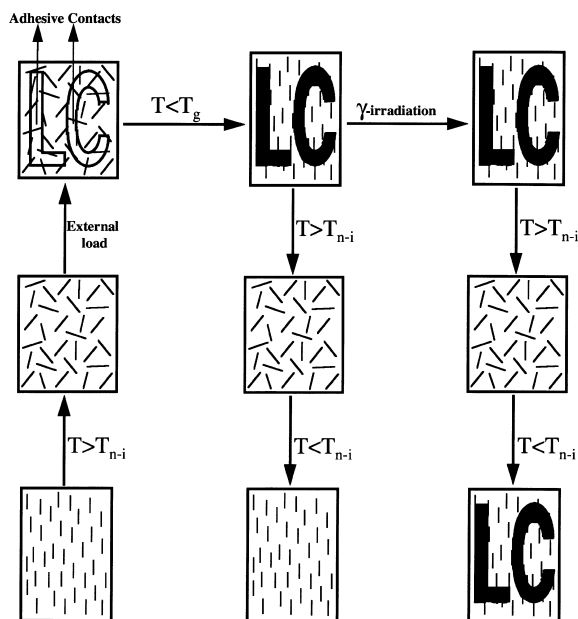
Fig. 14. A schematic route to LC films with the macroscopic memory effect via fixation of the current distribution of poly- and monodomain regions by γ-irradiation.

of the film fixates the current distribution of the director and the combination of poly- and monodomain regions on the macroscopic scale. The resultant sample preserves the recorded information at temperatures well above T_g. More importantly, the original symbol reversibly restores after the system is cooled down from isotropic state to nematic phase. In essence, isotropization erases the information, but the material 'remembers' it due to covalent fixation of chain conformations caused by gamma-irradiation. As an example, Fig. 15 shows optical micrographs of the film that was treated in the way just described. The recorded symbol completely disappears in isotropic state and precisely recovers after isotropic–nematic phase transition. Moreover, if necessary this 'permanent' symbol information can be erased if the film is first exposed to external stress resulting in uniform alignment and then irradiated again to lock in the 'new' monodomain structure. The process can be successfully repeated as long as the system contains sensitive fragments producing free radicals under the action of gamma-rays.

ly, the rest of the film restore monodomain alignment and remain optically transparent. Therefore, any symbol can be recorded on the film either by means of 'hand-writing' or via application of a mask. However, this symbol information irreversibly disappears if the sample is heated above the glass transition temperature. Nonetheless, the successive gamma-irradiation

Therefore, the described method suggests a new approach to lithography by using acrylate-based LC networks as memory carriers. Further exploration of these systems may produce a generation of advanced materials with a high potential for technological applications.
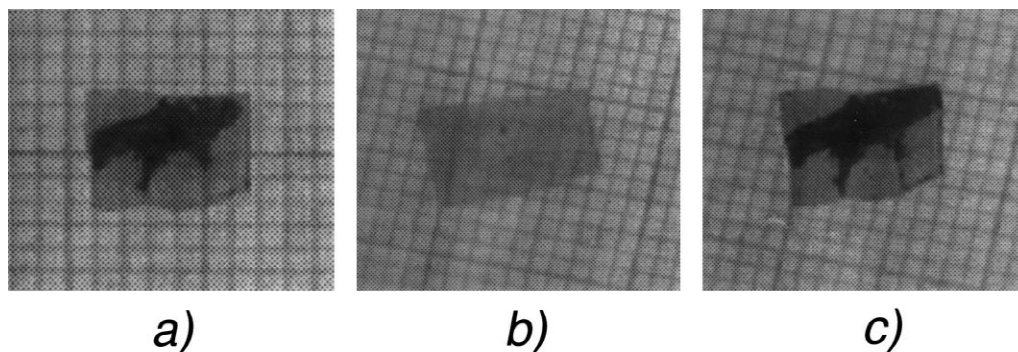

Fig. 15. Photographs of the LC film possessing macroscopic memory effect: (a) the sample obtained after γ-irradiation (RT); (b) photograph of the film in isotropic state at $T = 120°C$; (c) the sample after cooling to room temperature.

Acknowledgements

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